

The lowest three levels in each case are fully populated. A rough calculation using a value of $\beta_{MO} = 11,000 \text{ cm}^{-1}$, the above-mentioned ligand π -orbital energies, and other data from Barnum's work would indicate that Dq should be on the order of 200 cm^{-1} greater for daa than acac. The observed difference of 15 cm^{-1} is in the correct direction but is not sufficiently large to suggest that strong MO π bonding, extending through the entire ligand π system, need be invoked to rationalize the values of Dq . This suggests that the predominant electronic effect in these compounds is in the σ system, although not necessarily of a simple electrostatic nature.

TABLE II
ENERGIES OF π MOLECULAR ORBITALS IN
O-C-X-C-O COMPOUNDS^a

	X = CH	X = N	X = N-H
π_3	-1.574	-1.089	-0.927
π_4	-0.505	-0.505	-0.505
π_3	+0.712	+0.929	+1.234
π_2	1.605	1.605	1.605
π_1	1.961	1.959	2.293

^a Parameters: $\alpha_C = \alpha$; $\alpha_O = \alpha + 1.1\beta$; $\alpha_N = \alpha + 0.7\beta$; $\alpha_{NH} = \alpha + 1.5\beta$; $\beta_{CO} = \beta$; $\beta_{CN} = 0.8\beta$.

In spite of the crudeness of the Hückel approximation used in calculating the energies of the π levels of the ligands, they would seem to be qualitatively correct. The lowest energy ligand-ligand transition which is allowed in each case should correspond to the $\pi_3 \rightarrow \pi_4$ transition. From the spectra, it is obvious that the lowest energy allowed transition for $\text{Cr}(\text{daa})_3$ appears near $36,000 \text{ cm}^{-1}$ (doublet with maxima at $35,500$ and $37,000 \text{ cm}^{-1}$) compared to $29,650 \text{ cm}^{-1}$ for $\text{Cr}(\text{acac})_3$.²¹ The ratio of these frequencies is 1.21 which compares

very favorably with the predicted ratio of 1.18. The corresponding $\pi_3 \rightarrow \pi_4$ transition for diacetamide would then be expected near $43,200 \text{ cm}^{-1}$ and no intense transition is noted below $42,000 \text{ cm}^{-1}$ for this compound in chloroform.

A similar comparison may be made for $\text{Cr}(\text{dbm})_3$ and $\text{Cr}(\text{dba})_3$. The respective ligand field transitions at $17,600$ and $17,750 \text{ cm}^{-1}$ indicate that the substitution of phenyl for methyl lowers Dq slightly in each case. This is expected inasmuch as the inductive withdrawal of electronic charge by phenyl compared to methyl would lower the relative charge buildup on oxygen and thus provide a weaker ligand field. The relative energies of the ligand-ligand transitions also account for the distinctly different colors of the dbm and dba complexes. Conjugation of each of the ligand π systems with phenyl rings ought to shift the allowed $\pi \rightarrow \pi^*$ transitions to considerably lower energy compared to the methyl analogs. In fact, the lowest energy $\pi \rightarrow \pi^*$ transition at $25,850 \text{ cm}^{-1}$ for $\text{Cr}(\text{dbm})_3$ extends into the visible and thus imparts a gold-brown color to this solid. The first intense transition for $\text{Cr}(\text{dba})_3$ (maximum at $31,700 \text{ cm}^{-1}$; other maxima at $34,650$ and $36,900 \text{ cm}^{-1}$) is still fully contained in the ultraviolet region and as such does not influence the color of the solid which is identical with that of $\text{Cr}(\text{daa})_3$.

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(21) K. DeArmond and L. S. Forster, *Spectrochim. Acta*, **19**, 1393 (1963). These authors have demonstrated that this band and the other ultraviolet bands of $\text{Cr}(\text{acac})_3$ are most likely $\pi \rightarrow \pi^*$ transitions and not charge transfer in origin.

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Reactivity of Amines toward Cationic Gold(III) Complexes

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The influence of basicity upon the reactivity of substituted pyridines toward $[\text{AuCl}_4]^-$ does not change in going from methanol to acetone as solvent. The role of basicity in determining the nucleophilicity of the entering groups becomes greater when unipositive gold(III) complexes are used as substrates, and the nature of the groups bonded to the metal appears to affect strongly the relationship between the basicity and the reactivity.

Introduction

Some studies on the relationship between the reactivity of square-planar platinum(II) and gold(III) complexes and the properties of amines acting as either entering or leaving groups have been recently published.¹⁻³ Although "softness" is the most important

factor in determining the nucleophilicity of reagents toward Pt(II) substrates, it has been observed² that the "softness" of the amines, as felt by Pt(II), is not significantly affected by the nature of the groups attached to the nitrogen so that, in the replacement of the chloride in $[\text{Pt}(\text{bipy})\text{Cl}_2]$ by amines, it was possible to study the dependence of reactivity upon the basicity of the entering group. As expected, in the neutral Pt(II) complex the soft substrate cannot discriminate

(1) L. Cattalini and M. L. Tobe, *Inorg. Chem.*, **5**, 1145 (1966).
(2) L. Cattalini, A. Orio, and A. Doni, *ibid.*, **5**, 1517 (1966).
(3) L. Cattalini, M. Nicolini, and A. Orio, *ibid.*, **5**, 1674 (1966).

significantly between the various amines, and a slope of 0.06 has been obtained by plotting $\log k_2$ vs. pK_a . Moreover, in the same figure three parallel lines were drawn, each one corresponding to a different form of steric hindrance. The introduction of one or two methyl groups in the α position in substituted pyridines leads to an additive decrease in reactivity.

In going from $[\text{Pt}(\text{bipy})\text{Cl}_2]$ to the anionic $[\text{AuCl}_4]^-$ the same general behavior leading to linear free energy relationships between $\log k_2$ and pK_a have been observed.³ However, the value of the slope increases from 0.06 to 0.15 in spite of the presence of a negative charge on the substrate. These results strongly suggest that basicity becomes more important in determining nucleophilicity when the reaction center changes from Pt(II) to Au(III). This might be related to the inversion of lability between amine and chloride that is observed in nucleophilic displacement reactions on two series of Au(III) complexes, $[\text{Au}(\text{am})\text{Cl}_3]^+$ and *trans*- $[\text{Au}(\text{CN})_2(\text{am})\text{Cl}]$,⁴ in which it is always the amine and not the chloride that is replaced by the entering nucleophiles (Cl^- , Br^- , N_3^- , NO_2^-).

The increased influence of basicity, as well as the increase in reactivity of Au(III) complexes in comparison to Pt(II) complexes, is probably related to the difference in the effective nuclear charge and oxidation state.¹ However, no information is available about the influence of the total charge of the complex and of the nature of the groups bonded to the gold atom upon the relationship between basicity and reactivity.

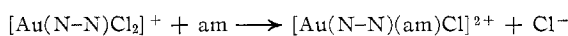
In the present paper we report the kinetics of the replacement of chloride in various unipositive chelated gold(III) complexes of the form $[\text{Au}(\text{N-N})\text{Cl}_2]^+$, where N-N is 2,2'-bipyridine, 1,10-phenanthroline, and 5-nitro-1,10-phenanthroline, by a series of substituted pyridines. The cationic gold(III) complexes undergo a relatively fast solvolysis in methanol, and so we have been forced to follow the reactions in acetone. Consequently, in order to compare the behavior of these complexes with that of $[\text{AuCl}_4]^-$ it has been necessary to repeat the kinetics with this complex in the new solvent and so these results also provide the first indication of the effect of the solvent on this type of process.

Results and Discussion

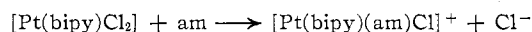
Preliminary studies of the spectra of the complexes in acetone indicate that they obey Beer's law, and no appreciable solvolysis is observed during the time necessary to follow the kinetics. Addition of LiNO_3 did not sensibly alter the rate constants, as might be expected in processes involving neutral entering groups.

Examination of the changing spectrum of acetone solutions originally containing $[\text{Au}(\text{N-N})\text{Cl}_2]^+$ and an excess of amine shows that a single-stage process is involved. Some kinetics have been followed by conductivity measurements. The molar conductivity at 25° increases with time in a first-order fashion, from ~ 130 to $\sim 250 \text{ ohm}^{-1} \text{ cm}^2$, as expected for a change

from a 1:1 to 1:2 electrolyte under these conditions ($10^{-4} M$). Since the initial spectra are those of the dichloro complexes, it is clear that the experimentally determined first-order rate constants are those of the replacement of one chloride



so that these reactions correspond to the reactions of the Pt(II) complex²



As far as the reactions with $[\text{AuCl}_4]^-$ are concerned, the products are the complexes $[\text{Au}(\text{am})\text{Cl}_3]$ previously described.^{1,3}

All of the processes follow the usual⁵ two-term rate law, $k_{\text{obsd}} = k_1 + k_2[\text{am}]$. The second-order rate constants, k_2 , for the replacement of one chloride by a substituted pyridine are collected in Table I, where, for comparison purposes, the data of the reactions of $[\text{AuCl}_4]^-$ in methanol are also reported. The values of k_1 do not appear in Table I; they are $k_1 < 10^{-4} \text{ sec}^{-1}$ for $[\text{AuCl}_4]^-$ and $[\text{Au}(5\text{-NO}_2\text{-phen})\text{Cl}_2]$, $k_1 = 1 (\pm 0.5) \times 10^{-3} \text{ sec}^{-1}$ for $[\text{Au}(\text{phen})\text{Cl}_2]^+$, and $k_1 = 8 (\pm 6) \times 10^{-4} \text{ sec}^{-1}$ for $[\text{Au}(\text{bipy})\text{Cl}_2]^+$. The uncertainty in k_1 is due to the fact that the process controlled by the k_2 is the most important one.

By plotting $\log k_2$ vs. the pK_a of the entering amine, as usual^{2,3} three parallel straight lines are obtained for each complex, any one line corresponding to a group of amines that have the same form of steric hindrance. (One example is reported in Figure 1.) Any substrate can be characterized by two parameters, the slope α and the separation Δ . Whereas one can consider α as arising mainly from electronic effects, Δ can be regarded as the steric effect due to the introduction of one methyl group *ortho* to the nitrogen in the entering pyridine, without any interference from the basicity change that might arise from the presence of this substituent.² The values of α and Δ obtained for each complex have been reported in Table II.

On comparing the behavior of $[\text{AuCl}_4]^-$ in methanol and acetone it is found that the rates of reaction decrease on going from the former to the latter (Table I) but it can be seen from the data in Table II that the relative parameters α and Δ are unchanged, indicating that the change in solvent influences all the reactions to the same extent. The rate constants change by 1.2 ± 0.05 in $\log k_2$ which corresponds to a decrease of $1.63 \pm 0.1 \text{ kcal/mole}$ in the free energy of activation on going from acetone to methanol. It may be possible that this arises from the hydrogen bonding between methanol and the developing chloride ion in the transition state, as has been suggested by Parker⁶ for certain organic substrates, but more work is necessary before this can be seriously considered for the $[\text{AuCl}_4]^-$ substrate.

On going from the anionic $[\text{AuCl}_4]^-$ to the cationic $[\text{Au}(\text{N-N})\text{Cl}_2]^+$ the value of α increases. This is in

(4) L. Cattalini, A. Orio, and M. L. Tobe, *Inorg. Chem.*, **6**, 75 (1967).

(5) C. H. Langford and H. B. Gray, "Ligand Substitution Process," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 18-54.

(6) A. J. Parker, *J. Chem. Soc.*, 1328 (1961).

TABLE I
SECOND-ORDER RATE CONSTANTS k_2 ($M^{-1} \text{ SEC}^{-1}$) FOR THE REPLACEMENT OF ONE COORDINATED
CHLORIDE BY AMINES IN GOLD(III) COMPLEXES (ACETONE, 25°)^{a,b}

Amine	pK_a^c	$[\text{AuCl}_4]^-^d$	$[\text{Au}(\text{bipy})\text{Cl}_2]^+$	$[\text{Au}(\text{phen})\text{Cl}_2]^+$	$[\text{Au}(5\text{-NO}_2\text{-phen})\text{Cl}_2]^+$
3-Cyanopyridine	1.38	(0.5)	...	0.03	...
3-Chloropyridine	2.84	(0.69)	...	0.0071	...
Pyridine	5.17	(1.6)	0.10	0.092	0.022
3-Methylpyridine	5.68	(2.0)	0.108	0.180	0.067
4-Methylpyridine	6.02	(2.1)	0.125	0.23	0.14
3,5-Dimethylpyridine	6.34	(2.5)	0.15	0.33	0.20
3,4-Dimethylpyridine	6.44	(2.9)	0.155	0.28	0.30
Quinoline	4.95	...	0.0096
2-Methylpyridine	6.10	(0.227)	0.0155	0.0155	0.0087
2,4-Dimethylpyridine	6.99	(0.325)	0.023	0.0395	0.0535
2,6-Dimethylpyridine	6.75	(0.03)	0.0022	0.002	0.0027
2,4,6-Trimethylpyridine	7.48	(0.0365)	0.00275	0.0044	0.0097

^a Values of the first-order rate constants as a function of amine concentration have been deposited as Document No. 9151 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints, or \$1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress. ^b The amine concentration was varied in the range 4×10^{-3} to $1 M$ and the concentration of the complexes was always less than $4 \times 10^{-4} M$. ^c The values of pK_a are for the acid conjugate to the amine in water. ^d The data in parentheses are for reactions in methanol, from ref 3.

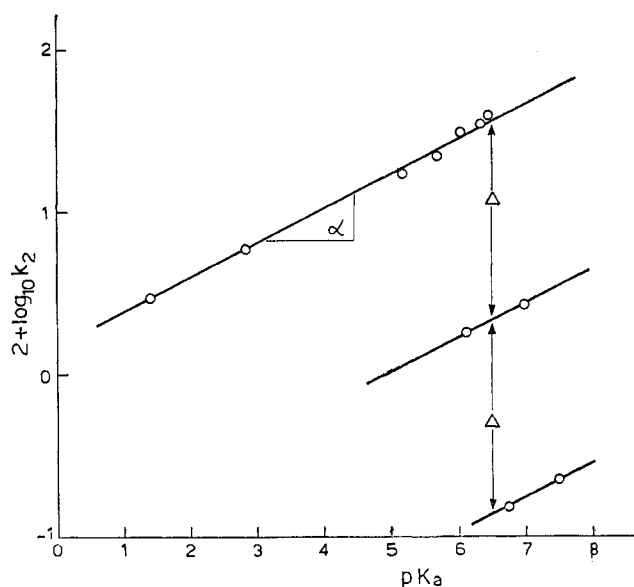


Figure 1.—Plot of $\log k_2$ against pK_a for the reactions of replacement of one chloride in $[\text{Au}(\text{phen})\text{Cl}_2]^+$ by substituted pyridines.

TABLE II
PARAMETERS α AND Δ FOR THE COMPLEXES STUDIED (IN
ACETONE AT 25°)

Complex	α	Δ
$[\text{AuCl}_4]^-$	0.15 (0.15) ^a	0.94 (0.96) ^a
$[\text{Au}(\text{phen})\text{Cl}_2]^+$	0.21	1.2
$[\text{Au}(\text{bipy})\text{Cl}_2]^+$	0.48	1.2
$[\text{Au}(5\text{-NO}_2\text{-phen})\text{Cl}_2]^+$	0.89	1.2

^a Data for the reactions in methanol (ref 3).

accord with the idea that the ability of the substrate to discriminate between different basicities increases when the negative charge at the reaction center decreases. However the greatest differences (Table II) appear to be due to the change in the nature of the chelate group. Haake and Cronin⁷ suggested that the chelate ring in $[\text{Pt}(\text{bipy})\text{Cl}_2]$ functions as a five-

membered aromatic ring. The same argument can also be applied to the isoelectronic gold(III) complexes and might result in a delocalization of charge from the reaction center. The increase of the slope α from 0.21 to 0.48 and 0.89 parallels the decrease of the basicity of the chelate groups, *i.e.*, $pK_a = 4.9 \rightarrow 4.4 \rightarrow 3.6$. If this is the reason for the differences between the cationic complexes, it means that the electronic displacement properties of the ligand bonded to the gold atom in the substrate have a much greater effect upon the relationship between basicity and reactivity than the effect due to the change in the total charge.

Finally a comment can be made on the values of Δ , which appear to be equal for the various cationic substrates but differ slightly from the value obtained for $[\text{AuCl}_4]^-$. It has been pointed out⁸ that steric hindrance in the transition state arises from the interactions between the entering group and the ligands that are in *cis* position to the leaving group in the four-coordinate planar substrate and become axial to the trigonal plane in the five-coordinate transition state. The heterocyclic chelate will interfere more with the methyl groups of the entering amine than will the chloride group.

Experimental Section

Materials.—The complexes $[\text{Au}(\text{bipy})\text{Cl}_2]\text{Cl}$ and $[\text{Au}(\text{phen})\text{Cl}_2]\text{Cl}$ have been obtained with the methods reported in the literature.^{8,9} $[\text{AuCl}_4]^-$ was reagent grade.

Dichloro(5-nitro-1,10-phenanthroline)gold(III) perchlorate was prepared by a slight modification of the above method. A 0.58-g sample of the ligand was dissolved in 50 ml of a water-ethanol mixture (5:1). The slow addition of 1 g of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in water solution to the stirred boiling solution produced a precipitate; the mixture was refluxed further for 30 min by which time much of the precipitate had dissolved and was then filtered. Sodium perchlorate was added to the solution and the perchlorate of the complex was immediately precipitated, filtered off, washed with a small quantity of cold water, ethanol, and petroleum ether (bp $30\text{--}50^\circ$), and dried in air. The ana-

(8) C. M. Harris and T. N. Lockyer, *J. Chem. Soc.*, 3083 (1959).

(9) C. M. Harris, *ibid.*, 682 (1959).

(7) P. Haake and P. A. Cronin, *Inorg. Chem.*, **2**, 879 (1963).

TABLE III
ANALYTICAL DATA FOR THE COMPLEXES OF THE TYPE $[\text{Au}(\text{N-N})\text{Cl}_2]\text{X}$

(N-N)	X ⁻	Au, %		C, %		N, %		H, %	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
1,10-phen	Cl ⁻	40.77	40.1	29.79	29.3	5.79	5.75	1.67	1.60
bipy	Cl ⁻	42.89	43.5	26.12	25.9	6.09	5.89	1.75	1.80
5-NO ₂ -1,10-phen	ClO ₄ ⁻	33.26	32.50	24.31	23.7	7.09	6.43	1.19	1.11

lytical data for all of the complexes required are collected in Table III. Acetone was purified and dried by successive distillation over KMnO_4 and K_2CO_3 , respectively. The substituted pyridines were commercial samples which were purified by distillation over KOH pellets.

Kinetics.—Freshly prepared solutions of the complex and the amine were brought to the reaction temperature separately and mixed in the thermostated cell of an Optica-CF4 double-beam recording spectrophotometer. The changes in optical density were followed by scanning the near-ultraviolet spectrum in the range 315–360 $\text{m}\mu$ at various times or, after preliminary experiments, by following the optical density change at a wavelength where

there was a maximum change and where rate constants could be conveniently calculated. All the experiments were carried out in the presence of an excess of amine in order to avoid possible equilibria and to have first-order kinetics. The observed rate constants for each experiment were calculated from the plot of $\log(D_\infty - D_t)$ against time. Some reactions were repeated several times under the same conditions and the reproducibility was better than 5%. Conductivity measurements were carried out by means of an LKB 3216B conductivity bridge.

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Multidentate Ligand Kinetics. X. Exchange Reactions of Metal(II)-Cyclohexylenediaminetetraacetate Complexes

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The exchange reactions of divalent metal ion complexes of *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetate (CyDTA) with aquometal ions are sluggish compared to the corresponding reactions of EDTA complexes. Nine metal(II)-CyDTA complexes are studied and in each case the rate of exchange is independent of the concentration of the aquometal ion and depends only upon the acid-dissociation rate of the complex. Second-order rate constants ($M^{-1} \text{sec}^{-1}$, 25°, 0.1 μ) for the reaction of hydrogen ion with metal(II)-CyDTA are 5.6×10^4 (Mg), 7.1×10^5 (Ca), 320 (Mn), 3.2 (Co), 3.5×10^{-4} (Ni), 3.9 (Cu), 170 (Zn), 23 (Pb), and 3.1 (Hg). The rate constants for Co, Ni, Cu, and Zn are consistent with a stepwise-dissociation path in which a proton adds to one of the CyDTA nitrogen atoms before the second metal-nitrogen bond breaks. Thus, the values for the rate constants are in remarkable agreement with values predicted from the characteristic water substitution rate constants of the metal ions and the CyDTA stability constants for hydrogen ion and the metal ions. In contrast Mn, Mg, and Ca depart significantly from this behavior and the rate constants are $1/10$ to $1/600$ as large as would be predicted. A mechanism is proposed for these complexes in which two metal-nitrogen bonds are broken in succession as a proton is added to one nitrogen. In this mechanism the water substitution rate constant of the metal ion is no longer applicable because several coordinate bonds are broken in the rate-determining step and the kinetics are not characteristic of a stepwise process.

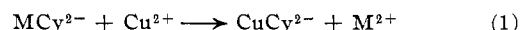
Introduction

The cyclohexane ring in CyDTA prevents this multidentate ligand from undergoing a process of simultaneous unwrapping and transfer of its coordinating groups from one metal ion to another which is characteristic of EDTA.^{1,2} Earlier papers in this series showed that nickel-CyDTA¹ and mercury-CyDTA³ complexes exchange with copper and other metal ions at a rate which depends on the hydrogen ion concentration but not on the concentration of aquometal ions. In the present work the CyDTA complexes of seven other divalent metal ions from various groups of the periodic table show the same type of kinetic behavior. The general exchange reaction with copper is

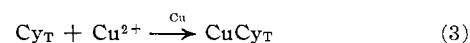
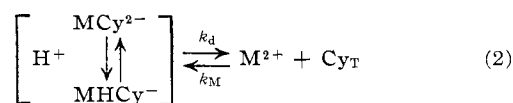
(1) D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **2**, 683 (1963).

(2) D. W. Margerum, D. L. Janes, and H. M. Rosen, *J. Am. Chem. Soc.*, **87**, 4463 (1965).

(3) D. L. Janes and D. W. Margerum, *Inorg. Chem.*, **5**, 1135 (1966).



where M^{2+} is Mg, Ca, Mn, Co, Ni, Cu (exchanging with Pb), Zn, Hg, or Pb, and Cy^{4-} is *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetate (CyDTA). However, no direct kinetic interaction between Cu^{2+} and MCy^{2-} is observed, and the kinetic system is



where $\text{Cy}_T = \text{Cy}^{4-} + \text{HCy}^{3-} + \text{H}_2\text{Cy}^{2-} + \text{H}_3\text{Cy}^-$ and $\text{MCy}_T = \text{MCy}^{2-} + \text{MHCy}^-$. A steady-state approximation is appropriate for Cy_T because its concentration is extremely small in the presence of excess copper ion. Equation 4 can be simplified to eq 5 if